TRANSITION METAL IONS AND HETEROGENEOUS NUCLEATION IN GLASS

FINAL REPORT
N 00014-67-A-0117-0017
NR 032-538 / 10-10-73 (471)

by

R. K. MacCrone
Division of Materials Engineering
Rensselaer Polytechnic Institute
Troy, New York
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Abstract

The research carried out during the tenure of the suppport is described. The work shows

(i) That the magnetic ions in the glasses studied (iron ions) are contained in well defined structures, namely diads and triads. The physical properties of these structures are described and the relevant parameters determined.

(ii) That during nucleation heat treatments, there is very little change in the structure of the glass as determined by magnetic measurements. Only oxidation of $Fe^{+2} \rightarrow Fe^{+3}$ takes place, but this seems to play a vital role in determining the final crystalline product phase.

(iii) On crystallization, Fe_3O_4, γ-Fe_2O_3 and some spinel form depending upon the temperature of nucleation. These phases determine the majority crystalline phase of the glasses.

In conclusion, there is much in the magnetic properties of these glasses that is imperfectly understood.

Finally, a list is given of students and research associates who worked on the project and their thesis abstracts. Also given are the abstracts of the technical reports and papers.

Introduction

This program of research into the mechanism of crystallization in glasses induced by the presence of nucleating agents was supported by the ONR from 1st January 1973 to 31st December 1975.

The essential feature of the work was to use a "magnetic" nucleating agent, in this case the oxide Fe_2O_3, and to study the atomic aggregation by monitoring the changes occurring in the magnetic and other parameters associated with magnetic ions. The magnetic ions in this case act as both nucleating agent and probe at the same time.

The two basic physical measurements made in this work were magnetic susceptibility, ac and dc, down to 50 mK and electron paramagnetic resonance. These physical measurements were coupled with real space and reciprocal space investigations of the morphology in an attempt to link the magnetic changes with the morphological changes.

Results

The major findings of the research are contained in the three technical reports, a publication and Ph.D. thesis and an M.S. thesis. The highlights of the work were presented at several technical meetings.

The technical reports, papers, theses are listed in Tables I, II and III, together with their abstracts for convenience.

The results may be put in perspective and summarized as follows:

1. The distribution of magnetic and other ions in glasses was generally considered to be fairly uniform. Our initial work on a non-crystallizing

glass showed that iron ions formed remarkedly characteristic structures on a microscopic scale, namely diads and triads of exchange coupled ions. The parameters pertaining to these entities J, TN, etc. could be fairly well determined, all the more remarkable since no use could be made of anisotropy.

2. In a crystallizable glass, these structures of diads and triads were also shown to exist in the quenched material, although their properties were not studied in the same detail as that previously described.

During nucleation, however, very little change in the glass structure took place as revealed by the physical measurements. In fact, the only changes that could be detected (by Mossbauer spectroscopy) was a gradual oxidation of $Fe^{+2} \rightarrow Fe^{+3}$ ions. Small angle X-ray measurements and optical micrographs also failed to detect any large scale variations in structure during the nucleation heat treatments.

3. The magnetic structures of a nucleated and crystallized glass followed a distinct pattern, a function of the nucleation temperature but not the crystallization temperature apparently.

As the nucleating temperature was progressively increased, so the magnetic structures that could be detected were Fe_3O_4, γ-Fe_2O_3 and some spinel; αFe_2O_3 or some alumino-ferrite. This strongly suggest that there may exist "amorphous" regions of these structures in the glass before crystallization, and the structure is determined by the Fe^{+2}/Fe^{+3} ratio. Since it is known that there are three major crystalline phases formed as a function of nucleating temperature (anorthite, wallastonite, spinel) this strongly suggests epitaxial nucleation on Fe_3O_4, γ-Fe_2O_3, spinel.

The crystallography of this possibility has not been studied.

Several novel features were observed during the work, namely a strong paramagnetic relaxation at low temperatures not due to superparamagnetic effects and a magnetic ordering at 2K, amongst others. These features presently are unfinished, awaiting further work.

Personnel

The following worked on the problem in one form or another. In all cases the individuals have proceeded onward in their careers and will contribute in industrial or academic research.

J. Aitken
Research Associate 1973-June 1974
Employed by I.B.M. at Watson Research Laboratory.

J. Williams
Research Associate June 1974-December 1975
Employed as lecturer, Physics Department, R.P.I.

D. W. Moon
Graduate Student Ph.D.
Employment pending at NASA

M. Boden
Graduate Student M.S.
Employed by Physics Department as lecturer, University of New Hampshire

L. Trombetta
Undergraduate Student
Application for graduate study pending at Cornell, M.I.T., Boston, Massachusetts

Table I

Technical Reports

No. 1, N 00014-67-A-0117-0017, NR 032-538 / 10-10-73 (471), January 1974

ABSTRACT

Magnetization measurements on x Fe_2O_3 (1-x) [BaO.4B_2O_3] glasses have been made over the temperature range from 50 mK to 300K for $0 < x < 0.10$. Electron paramagnetic resonance measurements were also made on the same specimens at the temperatures 300 and 77 K.

These structure sensitive measurements reveal that the majority of the iron ions exist in pairs (diads) and in groups of three, (triads). Only a minority of the iron follows a random distribution expected in a glass. The local crystalline nature of the triad structures is reflected in the very narrow spread in J values, inferred from computer calculations of "amorphous" triads.

The isolated Fe^{+3} concentration was obtained from the epr $g = 4.28$ resonance. The isolated ion concentration increased with x at first, passed through a maximum at $x \sim .03$ mole % and decreased fairly rapidly thereafter.

The existence of the triads was inferred from their magnetic susceptibility. This susceptibility was obtained by subtracting the theoretical magnetization of the isolated ions from the total measured value. This deduced magnetization attributed to the triads displayed precisely that expected for a group of three ions interacting antiferromagnetically with an exchange $J = 3.4 \times 10^{-4}$ eV.

On the assumption that the triads order at liquid helium temperatures with a resultant moment equal to one of the members, the concentration of isolated Fe^{+3} ions as a function of total Fe_2O_3 content was independently determined from magnetization measurements, and found to be in quantitative agreement with the epr measurements. At lower temperatures $\sim$ 1.8K, the resultant moment of the triads becomes "blocked."

No. 2, N 00014-67-A-0117-0017, NR 032-538 / 10-10-73 (471), January 1975

ABSTRACT

The magnetic susceptibility changes and the variations of the epr spectra of a CaO-MgO-Al_2O_3-SiO_2 glass have been studied during the Fe_2O_3 induced nucleation and crystallization.

The magnetic susceptibility of (mole %) 28.9 CaO-14.3 MgO-11.4 Al_2O_3-40.4 SiO_2 glass containing 5 mole % Fe_2O_3 has been measured over the temperature range 300K to 50mK in a variety of glass specimens. The epr spectra of these same specimens has been measured to 300K.

The glass specimens comprise the as-quenched glass, a set of glass specimens nucleated for two hours over the temperature range 650°C to 850°C, and a set of specimens crystallized for 25 minutes at 925°C after nucleation over the same temperature range.

From these measurements the first goal of a qualitative elucidation of the mechanism of catalyzed crystallization has been obtained, namely

(i) that clusters of Fe ions already exist in quenched glasses

(ii) on nucleation at lower temperatures the clusters clump together with little evidence of crystallinity

(iii) on nucleation at higher temperatures the clusters clump together with evidence of crystallinity

(iv) the Fe^{+2}/Fe^{+3} ratio decreases with increasing nucleation temperatures, and this oxidation state probably sets the crystalline phase observed after crystallization (see below)

(v) on crystallization, Fe_3O_4 or γ-Fe_2O_3 or MgFe AlO_4 form, depending upon the temperature of nucleation

(vi) the catalyzed crystallization of the major phase is apparently by the epitaxial growth around small cystallites of the above magnetic phases.

The experimental evidence is against the Gibbs approach of catalyzed crystallization, that is, an approach which assumes that the heterogeneous nucleant reduces the free energy between the nucleus and the matrix.

The work also contains a mini-review of crystallization in similar glass systems.

No. 3, N 00014-67-A-0117-0017, NR 032-538 / 10-10-73 (471), January 1976

ABSTRACT

A CaO-MgO-Al_2O_3-SiO_2 glass containing the nucleating catalyst Fe_2O_3 was subject to a series of nucleating heat treatments. Magnetic susceptibility measurements from room temperature to 50mK have been made

Table II

Theses

D. W. Moon Ph.D. 1975

A Magnetization study of the xFe_2O_3 $(1-x)$ $(BaO \cdot 4B_2O_3)$ Glass System

Abstract

D.C. magnetic susceptibility measurements on the glasses xFe_2O_3 $(1-x)$ $(BaO\ 4B_2O_3)$, for $0<x<0.10$ over the temperature range from room temperature to below liquid helium temperature, have been made.

The observed Curie constants are found to be smaller than the free ion values by about 35% for the 3 mole fraction of Fe_2O_3 glass up to about 40% for the 10 mole % Fe_2O_3 glass. The paramagnetic Neel temperatures also show significant deviations from zero value of the free ions; the observed paramagnetic Neel temperatures vary from about -5 K for the 3 mole % Fe_2O_3 glass to -25 K for the 10 mole % Fe_2O_3 glass.

These experimental results lead to the conclusion that magnetic iron ions are not randomly distributed in the glass as should be expected at these extremely dilute concentrations below the solubility limit. Instead, it has been inferred that the transition metal ions are arranged in groups of two and three as well as expected singles.

Iron ions within the pair and triad are interacting antiferromagnetically with the exchange integral, J, value from 10^{-3} to 10^{-2} eV.

M. Boden M.S. 1976

The AC Magnetic Susceptibility of a Glass Ceramic Containing Iron Oxide

Abstract

The dynamical magnetic susceptibility of a glass containing iron oxide was measured in the temperature range from 1.5°K to 77°K at frequencies between 3 and 30kHz. These measurements were made with a bridge of inductors, which is described, and a lock-in amplifier. A general survey of the major classes of magnetic materials and their response to a low frequency time dependent field is given. The measurements showed a Curie-Weiss susceptibility, but with a large loss angle which does not change with temperature. These results are explained in terms of the presence of both bound electrons, which give the Curie-Weiss susceptibility and conduction electrons, which through eddy currents cause the loss. This is supported by spin resonance measurements that were also made on the glass.

Table III

Papers

Magnetic Properties and Structure of xFe_2O_3, $(1-x)[BaO, 4B_2O_3]$ Glasses

Physics and Chemistry of Glasses, Vol. 16, No. 5, October 1975

Abstract

By using two structure sensitive techniques, namely magnetic susceptibility measurements from 0.05 to 300K and electron paramagnetic resonance measurements at 300 and 77K in xFe_2O_3, $(1-x)[BaO \cdot 4B_2O_3]$ glasses for $0 < x < 0.10$, it has been determined that at concentrations greater than about 3 mol% Fe_2O_3, the Fe^{3+} ions are not randomly distributed in the glass matrix as might be expected. On the contrary, the experimental results can be reasonably interpreted in terms of small magnetic structures. Iron ions exist predominantly as free ions, in pairs (diads) and in groups of three (triads); those within the diads and triads are coupled antiferromagnetically with J ranging from 10^{-3} to 10^{-2} eV.

on these samples, and the paramagnetic resonance down to 4K determined. The morphology of the specimens was concomitantly investigated using SAXS, optical microscopy and electron microscopy.

All the magnetic measurements above 2K failed to reveal any changes upon nucleation heat treatments. Magnetic susceptibility measurements below 2K showed systematic variations in the magnetic behaviour with nucleation. The structural variations responsible were not determined.

The morphological studies failed also to detect changes in "gross" structure during nucleation.

In conclusion, this study indicates that the mechanism of catalyzed crystallization in this glass is very subtle.

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